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Protonation of tetranuclear oxo(chloro)pyridinecopper(II) complexes by HBF_4 in nitrobenzene

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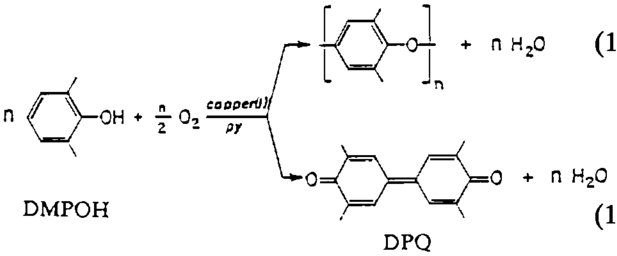
Abstract

Tetrafluoroboric acid (HBF_4) and triethylamine (Et_3N) have been added consecutively to solutions of tetranuclear oxocopper(II) complexes (μ_4-O)$py_3Cu_4Cl_4O$ (**Ia**), (μ_4-O)$py_4Cu_4Cl_4O$ (**Ib**), (μ_4-O)$py_4Cu_4Cl_6$ (**IIa**), (μ-O)$_2N_4Cu_4Cl_4$ (**IIIa**) and (μ_4-O)$N_4Cu_4Cl_6$ (**IVa**) in nitrobenzene at 25 °C to examine their proton basicities. Here, py is pyridine and N is *N,N*-diethylnicotinamide. The reactions were assigned from spectral and conductivity data. We conclude that the μ_4-oxo groups of **IIa** and **IVa** are reversibly monoprotonated by HBF_4 and are less basic than Et_3N. Further addition of HBF_4 apparently removes the central μ_4-oxo group of **IIa** and **IVa** as H_3O^+ and then protonates coordinated py and N. Complexes **Ia**, **Ib** and **IIIa** are irreversibly monoprotonated at their respective oxo groups, which are more basic than Et_3N. The protonation sequence for **Ia** consists of loss of its terminal oxo group Cu_v–O as H_3O^+, followed by loss of coordinated py as pyH^+. The sequence for **Ib** is the same except that py coordinated at the *v* site of **Ib** is protonated in preference to py at sites *x*. The μ_4-oxo group of **Ia** and **Ib** and the OH groups of diprotonated **IIIa** are less basic than their respective ligands py and N. Implications of the results on the mechanisms of copper-catalyzed phenolic oxidative coupling reactions are considered.

Introduction

The copper(I)–copper(II) couple is a versatile catalyst for biochemical and industrial reactions of O_2 [1–6]. It is the redox principle of polynuclear copper metalloenzymes in plants, lower animals and mammals [1, 2], several of which have been effectively modelled [2, 3]. Phenolic oxidative coupling reactions (1) are catalyzed in aprotic solvents by copper(I) halides CuX in the presence of *N*-alkyldiamines (L) or pyridine (py). The product distribution is sensitive to experimental conditions [4–6]. Optimization of reaction (1a) with particular CuX, L, py or DMPOH concentrations, solvents and temperature gives very useful poly(phenylene oxide) products [4, 5].

Halo-bridged, four-coordinate molecular dimers $[LCuX]_2$ are rapidly oxidized by O_2 in aprotic solvents to give oxocopper(II) dimers $[LCuX]_2O$ that initiate reactions (1) [7]. $[LCuX]_2O$ polymerize and self-destruct in the absence of substrates [7] but are stabilized as solid carbonatocopper(II) initiators by reaction with CO_2 [8].



(1a)

(1b)

Halo(py)copper chemistry is more complicated than with ligands L [9–13]. Copper(I) monomers py_3CuCl [9, 10], dimers $[py_2CuCl]_2$ [9] and tetramers $[pyCuCl]_4$ or $[py_2CuCl]_4$ [9] exist in aprotic solvents under different experimental conditions. Oxocopper(II) tetramers $py_3Cu_4Cl_4O_2$ (**Ia**) and $py_4Cu_4Cl_4O_2$ (**Ib**) (Scheme 1 [9, 11–14]) result from eqns. (2)–(5). Tetramers **Ia** and **Ib** initiate and catalyze reaction (1b) [11]. They react with excess py to give a soluble living polymeric form of copper(II) oxide, eqns. (6) and (7) [12, 13].

$$3py + 4CuCl(s) + O_2 \longrightarrow py_3Cu_4Cl_4O_2\ (\mathbf{Ia}) \tag{2}$$

$$4py + 4CuCl(s) + O_2 \longrightarrow [pyCuCl]_4O_2\ (\mathbf{Ib}) \tag{3}$$

$$[py_2CuCl]_4 + O_2 \longrightarrow \mathbf{Ib} + 4py \tag{4}$$

$$2[py_2CuCl]_2 + O_2 \longrightarrow \mathbf{Ib} + 4py \tag{5}$$

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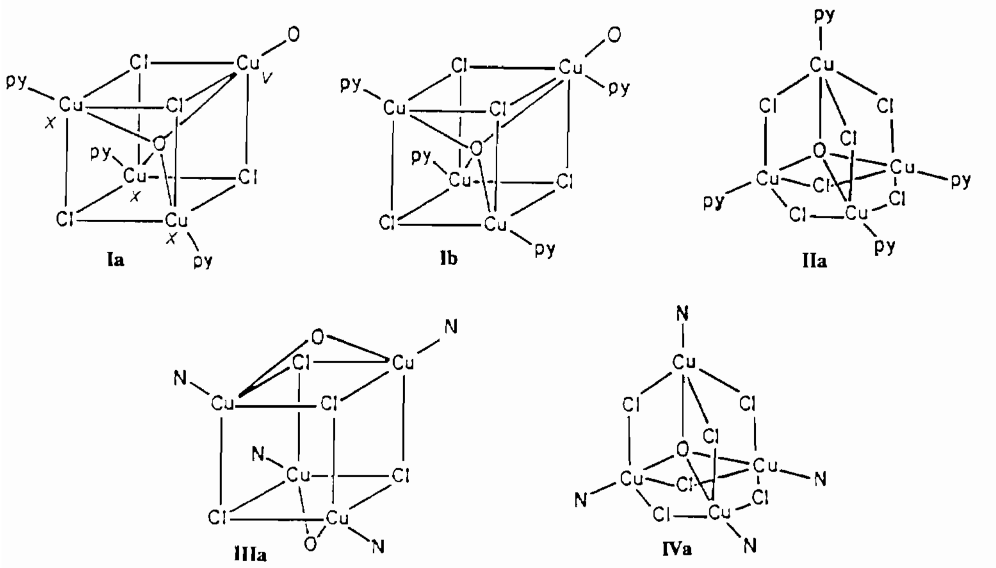


Ia **Ib** **IIa** **IIIa** **IVa**

Scheme 1.

$$\mathbf{Ib} + 4\mathrm{py} \longrightarrow 2\mathrm{py_2CuCl_2} + (\mathrm{py_2CuO})_2 \qquad (6)$$

$$n(\mathrm{py_2CuO})_2 \longrightarrow (\mathrm{py_2CuO})_{2n} \qquad (7)$$

Attempted isolation of solid **Ib** often gives crystalline decomposition product (μ_4-O)py$_4$Cu$_4$Cl$_6$ (**IIa**, Scheme 1 [15]), which is inactive in reaction (1) [9] and has much lower affinity for py than **Ib** [12].

Species **I** and [LCuX]$_2$O deprotonate phenols and their copper(II) centers oxidize the resulting phenolate [8, 9, 16]. Tetranuclear (μ_4-O)py$_3$Cu$_4$Cl$_4$(ODMP)$_2$ is the key intermediate of stoichiometric reaction (1b) in nitrobenzene. The equilibrium constant of reaction (8) is $(7 \pm 1) \times 10^7$ at 32 °C in nitrobenzene. Copper(I) reductant [pyCuCl]$_4$ is very weakly basic and has a much lower affinity than **I** for DMPOH, indicating that the most basic sites of **Ia** and **Ib** are their oxo groups. However, the μ_4-oxo group of **Ia** shows no sign of reversible protonation even at quite high DMPOH concentrations [11].

Reaction (9) is the rate-determining step in coupling process (1b) [11]. Equations (8) and (9) involve rapid and slow proton transfer from phenol to coordinated oxide, respectively. Co-product water interferes in some way with copper reoxidation reaction (3) so that reaction (1b) is stoichiometric at low or moderate phenol concentrations [11].

$$\mathbf{Ia} + 2\mathrm{DMPOH} \rightleftharpoons (\mu_4\text{-O})\mathrm{py_3CuCl_4(ODMP)_2} + \mathrm{H_2O} \qquad (8)$$

$$(\mu_4\text{-O})\mathrm{py_3CuCl_4(ODMP)_2} + \mathrm{py} \longrightarrow [\mathrm{pyCuCl}]_4 + \mathrm{DPQ} + \mathrm{H_2O} \qquad (9)$$

Changing the ligand on copper from py to *N,N*-diethylnicotinamide (N) has the following results: (i) [NCuX]$_4$ (X = Cl or Br) are much more soluble than [pyCuX]$_4$ [9]; (ii) [NCuX]$_4$ and their oxidation products [NCuX]$_4$O$_2$ (**III**, Scheme 1) have very low affinity for added N and form dicarbonato derivatives with CO$_2$ [9]; (iii) **III** and their carbonato derivatives can be isolated as redissolvable solids [9]; (iv) the electronic spectra of **III** are insensitive to solvent, but solvent nitrobenzene intensifies the spectra of polar molecules **Ia** and **Ib** [14]; (v) [NCuX]$_4$O$_2$ are not initiators for reactions like (1) [9, 14, 16].

Different dispositions of the two oxo groups in **I** and **III** (Scheme 1) are indicated by a variety of evidence [7, 11, 17]. The proposed terminal oxo group of **I** is expected to be much more basic [18] than the μ-oxo units of **II** and **III**. Attempted crystallization of **IIIa** (X = Cl) gives crystalline **IVa** [19] (Scheme 1). Molecules **IIa** and **IVa** have virtually identical core structures with equivalent copper(II) sites [15, 19].

Reaction (1a) can be optimized [4–6] but the origin of the effects is obscure, particularly at high py and DMPOH concentrations. Anion DMPO$^-$ is an excellent ligand for **Ia** [11] and high [DMPOH] could change the nuclearities of the copper(II) components to favor dimers and monomers. Increasing [DMPOH] also increases the overall acidity of the system, which is an important consideration for oxocopper(II) complexes [13].

In this paper, the proton basicity of tetranuclear oxocopper(II) complexes **Ia**, **Ib**, **IIa**, **IIIa** and **IVa** in nitrobenzene has been investigated by consecutively adding HBF$_4$ (a strong acid with a weakly coordinating anion [3]) and triethylamine (Et$_3$N, a strong base and poor ligand [20]) as the competing reference base. We conclude that the protonation sequences of the core structures in Scheme 1 are different and distinguishable.

Experimental

Materials

Solvent nitrobenzene (Aldrich) was distilled under vacuum from P_2O_5 and stored over 4 Å molecular sieves. Pyridine (Aldrich) was dried over KOH for 24 h, distilled from BaO and stored in the dark over 4 Å molecular sieves. Copper(I) chloride was prepared by the literature method [21]. High purity N_2 was deoxygenated by passage through a freshly activated column of Alfa DE-OX catalyst. The acid $HBF \cdot OEt_2$ and base Et_3N (Aldrich) were used as supplied. Their purity was confirmed by titration with standard, carbonate-free NaOH with phenolphthalein as indicator and by gas chromatography, respectively. Solutions of $[pyCuCl]_4$, **Ia** and **Ib** in nitrobenzene [11, 14] and solid products **IIa** [15], **IIIa** [9] and **IVa** [19] were obtained as previously described.

Titration procedures

Standard solutions of tetranuclear oxocopper(II) reactants **Ia**, **Ib**, **IIa**, **IIIa** and **IVa** (X=Cl throughout) (1.45 or 2.90 mM) in nitrobenzene were treated with standard solutions of HBF_4 and Et_3N (7.25 mM) in nitrobenzene. The spectrum of the product solution after each addition was immediately measured in the region 600–900 nm, which is where the oxocopper(II) reactants have characteristic absorption [9, 14]. All spectra were recorded with a computer-controlled Perkin-Elmer Lambda 4B spectrophotometer in matched quartz cells at 25 °C with standard procedures [12, 19]. The conductivities of all solutions were measured with a Beckman Instruments model RC-216B conductivity bridge at 50 c.p.s. The cell had 1 cm^2 Pt electrodes and a cell constant at 25 °C of 0.004147, as determined with a saturated aqueous solution of KCl.

The maximum error in our spectral and conductivity data is ±1%.

Results and discussion

General observations

Tetranuclear complexes **I**–**IV** (Scheme 1) contain two, one, two and one oxo groups, respectively. General principles would indicate that the μ_4-oxo group of **IIa** and **IVa** is the least basic because it is bonded to four equivalent copper(II) centers [15, 19]. The most basic site of the series is expected to be the proposed terminal oxo group of **Ia** and **Ib**: as emphasized by Mayer [18], the bond between copper(II) sites v and oxide in complexes **I** should be very ionic because every d orbital of copper(II) (d^9) is occupied. As a result, the oxide at site v in **I** formally has at least three lone pairs of electrons. With these same principles, the two μ-oxo groups of **III** should have intermediate basicity, especially if the Cu–O–Cu angle is not too acute. The other basic sites are the py and N ligands of **I**–**IV**, which could be the first sites to be protonated. For this reason, we first studied the protonation and deprotonation of **IIa** and **IVa**, whose molecular structures are known [15, 19].

*Reactions of (μ_4-O)$py_4Cu_4Cl_6$ (**IIa**) and (μ_4-O)-$N_4Cu_4Cl_6$ (N=N,N-diethylnicotinamide, **IVa**) with HBF_4 and Et_3N in nitrobenzene*

The copper(II) centers of **IIa** and **IVa** have trigonal bipyramidal geometry, with three halides in the equatorial plane and the central oxo group and py or N as axial ligands [15, 19]. Their electronic spectra in nitrobenzene consist of intense, overlapping maxima at 775 and 850 nm and a deep absorption minimum near 600 nm (Fig. 1).

Addition of 1 equiv. of HBF_4 to **IIa** in nitrobenzene causes an absorptivity decrease of about 10% that is

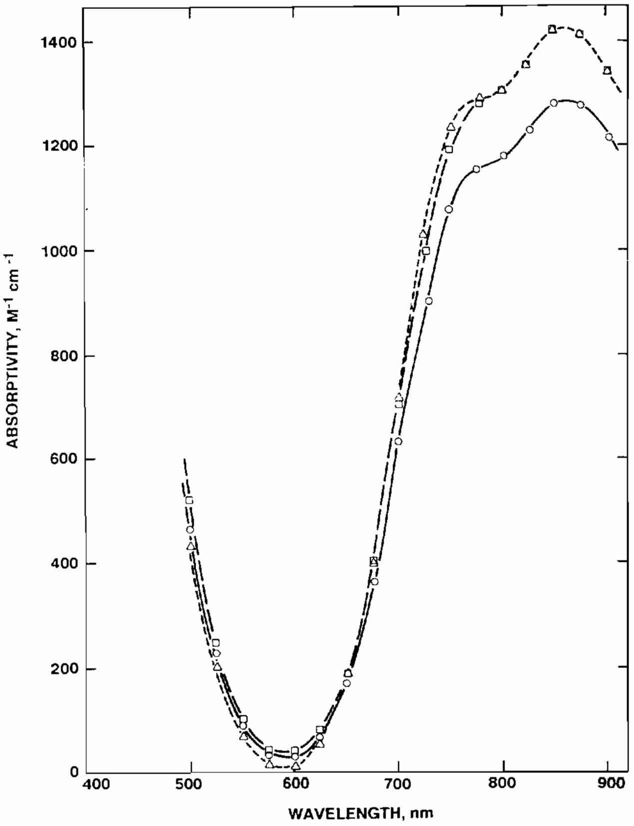


Fig. 1. Electronic spectra of **IIa** (△); **IIa**+1 equiv. HBF_4 (○); and **IIa**+1 equiv. HBF_4+1 equiv. Et_3N (□) in nitrobenzene at 25 °C.

reversed by addition of 1 equiv. of strong base Et_3N. An isosbestic point near 650 nm and little absorptivity change near 600 nm (Fig. 1) indicate reversible monoprotonation of **IIa** and that Et_3N is more basic than **IIa**. Addition of 2 equiv. of HBF_4 to **IIa** causes a larger absorptivity decrease at 700–900 nm and an absorptivity increase at 600 nm (Fig. 2). Most importantly, addition of 2 equiv. of Et_3N to the product solution does not regenerate the original spectrum (Fig. 2). In fact, the result of the Et_3N addition closely resembles the result of addition of 1 equiv. of HBF_4 (Fig. 1), indicating protonation of the μ_4-oxo group of **IIa** in preference to protonation of the coordinated py.

Addition of 3 equiv. of HBF_4 causes a yet larger absorptivity decrease at 850 nm but little change at 600 nm (Fig. 3). Again, addition of 3 equiv. of Et_3N to the product solution gives a spectrum resembling that from addition of 1 equiv. of HBF_4 and does not regenerate **IIa**. It is obvious from the minimum absorptivities in Figs. 1–3 that the product of addition of 2 equiv. of HBF_4 to **IIa** has a 600 nm spectral feature not found in the other species. We found that the behavior of **IVa** in the same experiments was closely similar to that of **IIa**. Reversible removal of one py or N (as pyH^+ or NH^+) with 1 equiv. of HBF_4 is hard to accept because of the irreversible results of addition of 2 or 3 equiv. of HBF_4 and the equivalent copper(II) sites of **IIa** and **IVa** [15, 19].

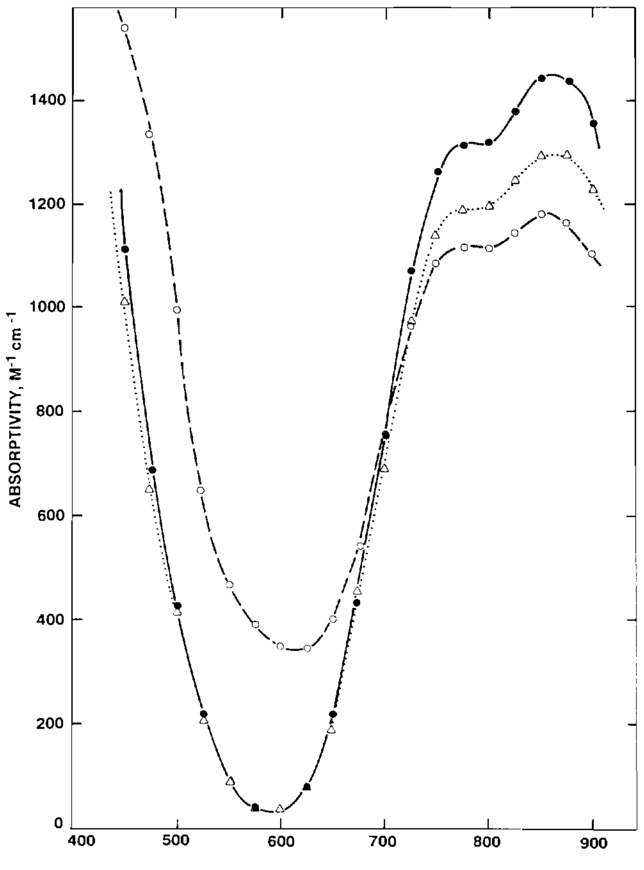


Fig. 2. Electronic spectra of **IIa** (●); **IIa** + 2 equiv. HBF_4 (○); and **IIa** + 2 equiv. HBF_4 + 2 equiv. Et_3N (△) in nitrobenzene at 25 °C.

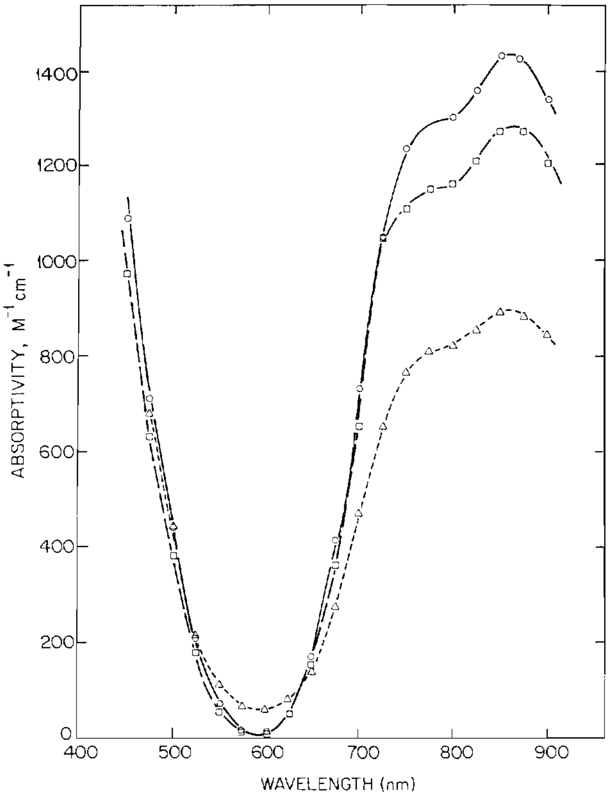
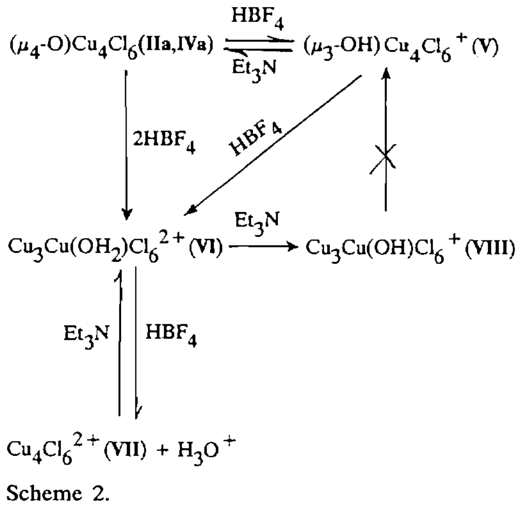


Fig. 3. Electronic spectra of **IIa** (○); **IIa** + 3 equiv. HBF_4 (△); and **IIa** + 3 equiv. HBF_4 + 3 equiv. Et_3N (□) in nitrobenzene at 25 °C.



Scheme 2.

Our results and proposed products are summarized in Scheme 2. Coordinated py and N are omitted because there is no evidence for their protonation in the earliest stages of the titration (*vide infra*). Tetrafluoroborate and ion-pair co-product Et_3N^+,BF_4^- also are omitted to clarify discussion.

We propose that addition of one proton to **IIa** or **IVa** gives **V** containing a central OH group that presumably is bonded to at least three of the four copper(II) centers. This group may be pseudo-spherical because of rapid intramolecular proton transfer in **IIa** and **IVa**. It is deprotonated by Et_3N to regenerate **IIa** or **IVa**. Addition of one proton to **V** converts this central group to water. We propose that this water molecule leaves the molecular core and is coordinated as a terminal aquo ligand by one of the four copper centers in **VI**. This aquo ligand is deprotonated by Et_3N to give **VIII** containing an OH group that could be bridging (bridging OH would help to explain the similar spectra of **V** and **VIII**).

Products **V** and **VIII** are not interconvertible. Reversible protonation of **VI** gives **VII**, which could be the ion-pair $py_4Cu_4Cl_6^{2+},H_3O^+$, with H_3O^+ associated with the Cl or py ligands. The spectra in Figs. 1–3 indicate that all the species in Scheme 2 contain copper(II) centers bonded to three chlorine atoms [22], which evidently are very weak proton bases. There is no spectral evidence for breakdown of the reactant core to give trimers or dimers.

Figure 4(c) shows the absorptivity decreases that occur at 850 nm on addition of up to 9 equiv. of HBF_4 to **IIa** and **IVa** in nitrobenzene. A distinct change of slope occurs on addition of the fourth proton to **IIa** and from this point the absorptivity decreases linearly with increasing $[HBF_4]$. The linear decrease is consistent with formation of products with the same nuclearity as the reactants but containing progressively fewer ligands py or N. The changes between 3 and 6 equiv. of added HBF_4 are less obvious for **IVa**, probably because coordinated N is less basic than coordinated py. However, the lines from 4 to 8 equiv. of added HBF_4 (**IIa**) and from 6 to 9 equiv. of added HBF_4 (**IVa**) are parallel (Fig. 4(c)), consistent with pyH^+ and NH^+ loss after protonation of the μ_4-oxo group of **IIa** and **IVa**.

The spectral measurements are supported by the conductivity data in Fig. 5. The conductivity of **IIa** increases linearly up to addition of 3 equiv. HBF_4, where a sharp change of slope is observed. Further addition of HBF_4 causes linear changes that are assigned to an increasing concentration of ion pairs pyH^+,BF_4^-. The changes are again less obvious for **IVa**, but the data indicate that seven protons are required for its complete protonation. Based on this information, the stoichiometry of complete reaction of **IIa** and **IVa** with HBF_4 is given by eqn. (10). This stoichiometry would predict that the spectra of the product solutions from **IIa** and **IVa** would be identical. The fact that they are not (Fig. 4(c)) is probably the result of different kinds and degrees of ion-pairing of pyH^+ and NH^+ with $Cu_4Cl_6^{2+}$ and BF_4^- (see the conductivity differences in Fig. 5).

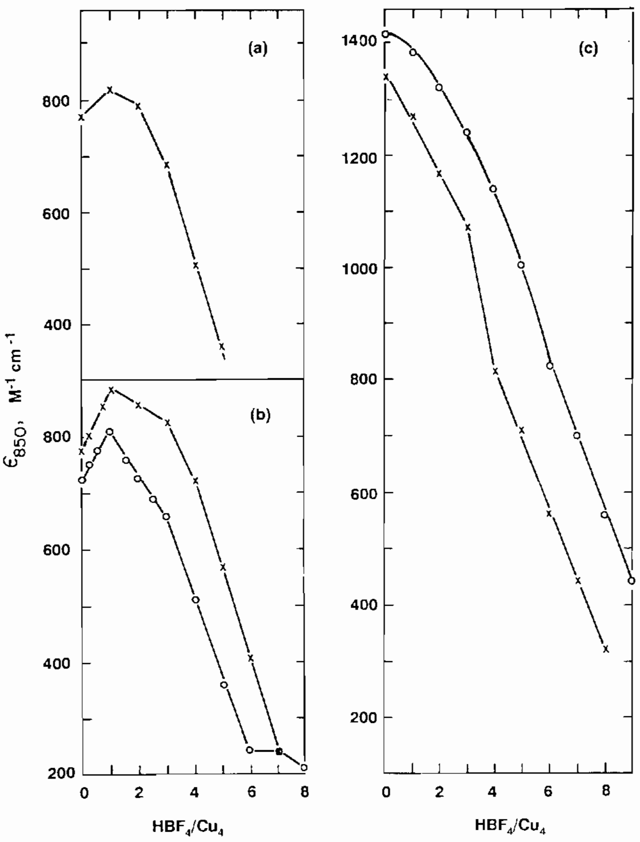


Fig. 4. Spectrophotometric data for titration of the following complexes with HBF_4 in nitrobenzene at 25 °C: (a) **IIIa**; (b) **Ia** (O) and **Ib** (x); (c) **IIa** (x) and **IVa** (O).

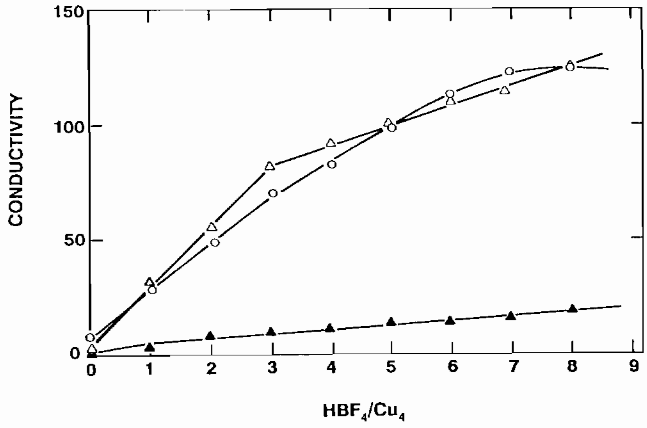


Fig. 5. Conductivity changes in the titration of **IIa** (△) and **IVa** (O) with HBF_4 in nitrobenzene at 25 °C. Also shown are the conductivities of HBF_4 solutions at the respective concentrations used for the titrations.

$$\text{IIa or IVa} + 7HBF_4 \longrightarrow Cu_4Cl_6^{2+},2BF_4^- + H_3O^+,BF_4^- + 4(pyH^+,NH^+),BF_4^- \quad (10)$$

Reactions of (μ-O)$_2$[NCuCl]$_4$ (IIIa) with HBF$_4$ and Et$_3$N in nitrobenzene

Solid tetranuclear complex (μ-O)$_2$[NCuCl]$_4$ (**IIIa**) is obtained from eqn. (11) and evaporation of the methylene chloride solvent [9]. Attempted crystallization of **IIIa** results in disproportionation to crystalline **IVa** [19]. Molecule **IIIa** is the only complex in Scheme 1 that forms a dicarbonato derivative by reaction with excess CO_2 [9, 14]. Reaction (12) indicates that **IIIa** contains equivalent μ-oxo groups that can open to accommodate the linear bridging requirements in known carbonatocopper(II) complexes [8]. The solid state EPR spectrum of **IIIa** indicates a square-planar copper(II) geometry [23].

$$[NCuCl]_4 + O_2 \longrightarrow \textbf{IIIa} \quad (11)$$

$$\textbf{IIIa} + 2CO_2 \longrightarrow (\mu\text{-}CO_3)_2[NCuCl]_4 \quad (12)$$

Complex **IIIa** has an intense electronic spectrum with overlapping maxima at 775 and 850 nm and a deep absorptivity minimum at 600 nm (Fig. 6). A small increase of absorptivity occurs on addition of 1 equiv. of HBF_4 to **IIIa** in nitrobenzene. A slight further absorptivity increase at 775 nm and a decrease at 850 nm occur on addition of 1 equiv. of Et_3N to the product solution. However, the result of this experiment is a solution with much more pronounced absorptivity at 600 nm (Fig. 6). Monoprotonation of **IIIa** is thus irreversible, in sharp contrast to the properties of **IIa** and **IVa** (see above).

The spectral changes caused by addition of 2 equiv. of HBF_4 also are not reversed by Et_3N, indicating that the μ-oxo groups of **IIIa** are more basic than Et_3N. Proposed species **X** containing bridging OH (Scheme 3, copper ion-pairs and NH^+,BF_4^- co-product are omitted) is consistent with the presence of hydroxo groups that are not deprotonated by Et_3N, as found for species **VIII** in Scheme 2.

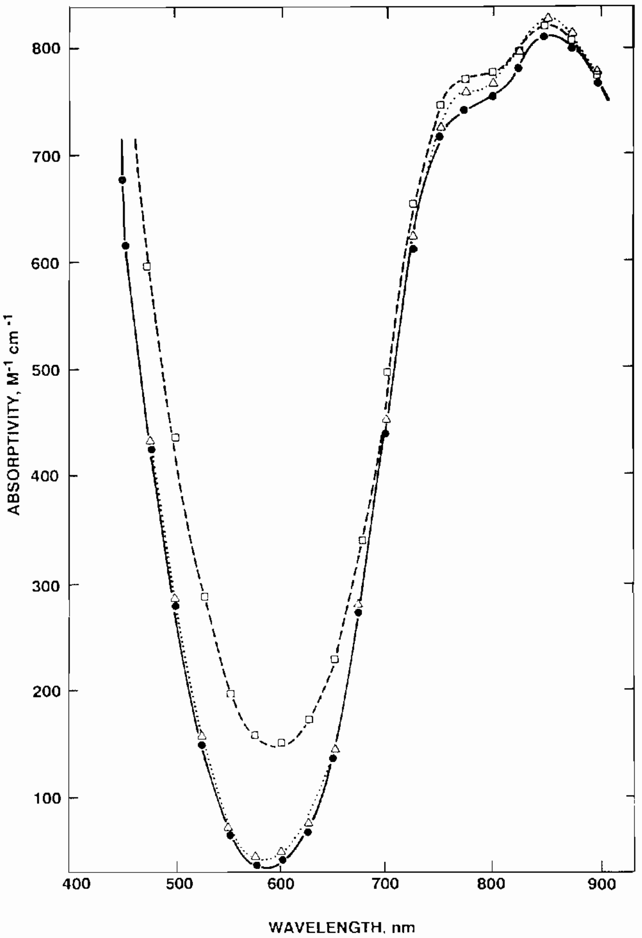


Fig. 6. Electronic spectra of **IIIa** (●); **IIIa** + 1 equiv. HBF_4 (△); and **IIIa** + 1 equiv. HBF_4 + 1 equiv. Et_3N (□) in nitrobenzene at 25 °C.

$$\begin{tikzcd}
(\mu\text{-}O)_2N_4Cu_4Cl_4(\text{IIIa}) \arrow[r, "HBF_4"] & (\mu\text{-}OH,\mu\text{-}O)N_4Cu_4Cl_4^{+}(\text{IX}) \arrow[d, "HBF_4"'] \\
 & (\mu\text{-}OH)_2N_4Cu_4Cl_4^{2+}(\text{X}) \arrow[d, "4HBF_4"'] \\
 & (\mu\text{-}OH)_2Cu_4Cl_4^{2+}(\text{XI}) + 4NH^{+}
\end{tikzcd}$$

Scheme 3.

The absorptivity changes which occur at 850 nm on addition of upto 5 equiv. of HBF_4 to **IIIa** in nitrobenzene are shown in Fig. 4(a). Complexes **IIIa** and **X** (Scheme 3) have similar absorptivity at 850 nm but that of **IX** is slightly larger. Further addition of HBF_4 to **X** causes a linear absorptivity decrease that parallels that observed in the last stages of protonation of **IVa**, identifying it as due to loss of coordinated N as NH^+. Conductivity data (Fig. 7) show sharp changes of slope at 3 and 6 equiv. of added HBF_4 that indicate the overall protonation stoichiometry of eqn. (13). Product **XI** is the dihydroxo analogue of the copper(II) product **VII** in Scheme 2 and eqn. (10). It is noteworthy that the OH groups of **XI** are less basic than coordinated N.

$$\textbf{IIIa} + 6HBF_4 \longrightarrow (HO)_2Cu_4Cl_4^{2+},2BF_4^- + 4(NH^+,BF_4^-) \quad (13)$$

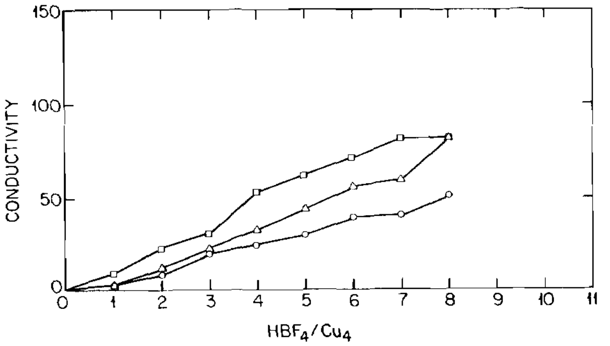


Fig. 7. Conductivity changes in the titration of **Ia** (□); **Ib** (△); and **IIIa** (○) with HBF_4 in nitrobenzene at 25 °C.

Reactions of (μ_4-O)py_3CuCl_4O (Ia) and (μ_4-O)-py_4CuCl_4O (Ib) with HBF_4 and Et_3N in nitrobenzene

Tetranuclear dioxocopper(II) complexes **Ia** and **Ib** are the only species in Scheme 1 that initiate and catalyze reaction (1b) [9–16].

Addition of 1 equiv. of HBF_4 to **Ia** causes a slight absorptivity increase at 775–900 nm and a decrease at 580 nm (Fig. 8). These changes appear to be reversed by addition of 1 equiv. of Et_3N. This result is unexpected because species **XII** (Scheme 4, BF_4^- omitted) should be a weak acid on the basis of the results for **IIIa** and earlier considerations.

The apparent reversibility could be due to weak coordination of Et_3N at the v site of **Ia**, which reacts with 1 mol of py to give **Ib** [14]. This explanation is supported by the result of further addition of HBF_4 and Et_3N to **Ia**. Addition of 3 equiv. of HBF_4 reduces the absorptivity of **Ia** at 850 nm by about 40% (Fig. 8), but attempted deprotonation of the product with 3 equiv. of Et_3N gives a spectrum with a maximum absorptivity of 640 M^{-1} cm^{-1}, to be compared with 710 M^{-1} cm^{-1} for **Ia** (Fig. 8). Et_3N may be a ligand for **Ia**, presumably by coordination at Cu_v [14]. However, it is certain that addition of more than 1 equiv. of HBF_4 to **Ia** is irreversible, consistent with the large equilibrium constant for reaction (8) [11].

Titration of **Ia** with HBF_4 causes a linear increase of absorptivity at 850 nm up to 1 equiv., then a linear decrease to 3 equiv. of added HBF_4 and then a sharper linear decrease on addition of further HBF_4 (Fig. 4(b)). The slope of the last titration stage is close to that of the last stage of protonation of **IIa** and corresponds to loss of pyH^+. The data in Fig. 4(b) indicate the overall stoichiometry of eqn. (14). It is noteworthy that the μ_4-oxo group of **XIII** is less basic than py at sites x. We recall that there is no evidence for significant protonation of the μ_4-oxo group of (μ_4-O)$py_3Cu_4Cl_4(ODMP)_2$ at quite high DMPOH concentrations [11].

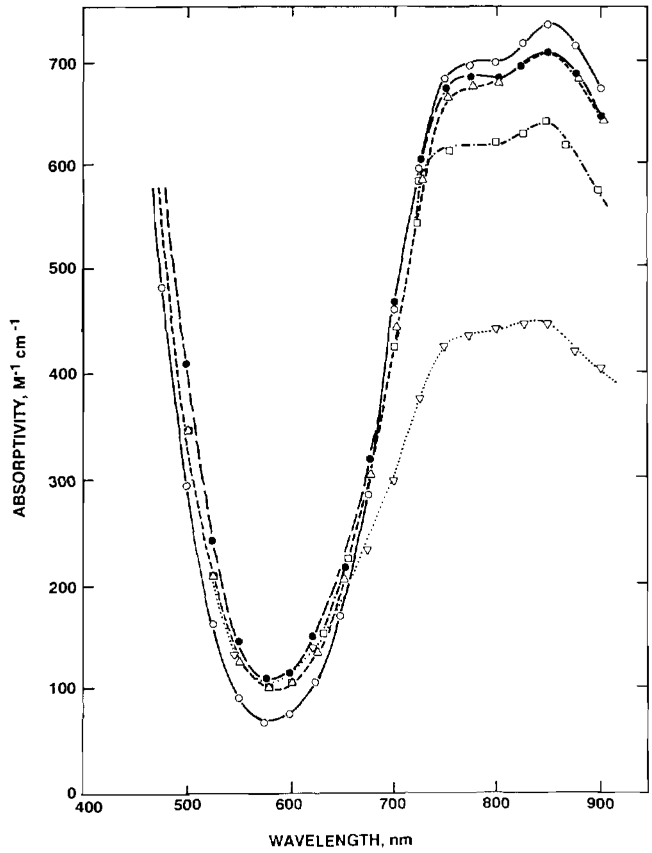
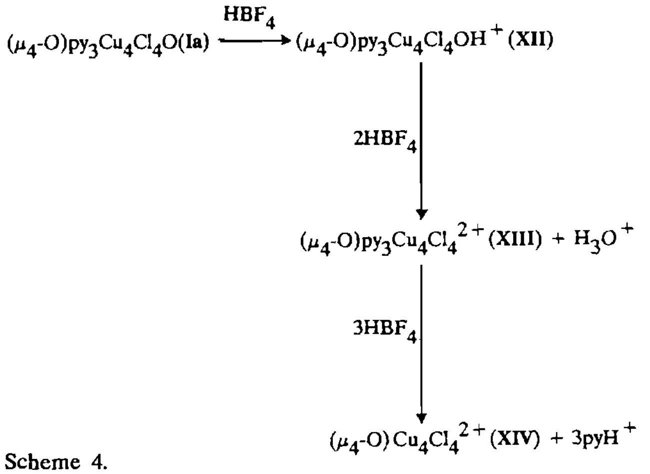


Fig. 8. Electronic spectra of **Ia** (●); **Ia**+1 equiv. HBF_4 (○); **Ia**+1 equiv. HBF_4+1 equiv. Et_3N (△); **Ia**+3 equiv. HBF_4 (▽); and **Ia**+3 equiv. HBF_4+3 equiv. Et_3N (□) in nitrobenzene at 25 °C.



Scheme 4.

$$\mathbf{Ia} + 6HBF_4 \longrightarrow (\mu_4\text{-O})Cu_4Cl_4^{2+},2BF_4^- + H_3O^+,BF_4^- + 3pyH^+,BF_4^- \quad (14)$$

Our results indicate that the most basic site of **Ia** is its proposed Cu_v–O group. Species **XIII** (Scheme 4) apparently contains a Cu_v–OH group. This hydroxo group is lost as the ion-pair H_3O^+,BF_4^- on diprotonation of **XII**, as indicated by the sharp conductivity increase after addition of 3 equiv. of HBF_4 (Fig. 7). We have not detected the protonation of $(\mu_4\text{-}O)Cu_4Cl_4{}^{2+}$.

The behavior of **Ib** parallels that of **Ia** (Fig. 4(b)) except for the stage from 3 to 4 equiv. of added HBF_4, which is assigned to protonation of the py ligand at the Cu_v site of **Ib** (Scheme 1). This py ligand evidently is more weakly coordinated and basic than py at sites *x*, consistent with its preferential displacement by ligands like *N*,*N*,*N′*,*N′*-tetraethylethylenediamine [14]. The conductivity changes on titration of **Ib** are smaller and less abrupt than those of **Ia** (Fig. 7), but a sharp conductivity increase occurs after 7 equiv. have been added and the species obtained by addition of 8 equiv. of HBF_4 to **Ia** and **Ib** are the same (Figs. 4(b) and 7). The overall stoichiometry of protonation of **Ib** by HBF_4 in nitrobenzene is thus given by eqn. (15).

$$\mathbf{Ib} + 7HBF_4 \longrightarrow (\mu_4\text{-}O)Cu_4Cl_4{}^{2+},2BF_4{}^- + H_3O^+,BF_4{}^- + 4pyH^+,BF_4{}^- \quad (15)$$

Conclusions

The terminal oxo group of **Ia** and **Ib** and the two equivalent μ-oxo groups of **IIIa** are irreversibly protonated by HBF_4 in preference to their coordinated py and N ligands. These oxo groups are more basic than Et_3N. Coordinated py at site *v* in **Ib** is more basic than py at sites *x*. In contrast, the μ_4-oxo groups of **IIa** and **IVa** are less basic than Et_3N and are reversibly monoprotonated by HBF_4. They are irreversibly diprotonated in preference to coordinated py or N.

Our results with HBF_4 as the reference acid and Et_3N as the competing base thus indicate the basicity order terminal-O, $\mu\text{-O} \gg \mu_4\text{-O}$ for protonation of the oxo groups in **I–IV**. Highest basicity for the terminal oxo group of **Ia** and **Ib** is indicated by the large equilibrium constant of eqn. (8) [11] and the inactivity of **IIIa** in reactions (1). Phenol DMPOH is the weak reference acid in this comparison. Formation of copper-coordinated phenolate is the key to initiation of reaction (1a) [11].

The μ_4-oxo group of **Ia** and **Ib** and the μ-oxo groups of **IIIa** evidently are not basic enough to deprotonate moderate amounts of excess DMPOH. This helps to account for stoichiometric, intramolecular reaction (9) [11]. However, the μ_4-oxo group and the coordinated py ligands of catalytic intermediate $(\mu_4\text{-}O)py_3Cu_4Cl_4(ODMP)_2$ could deprotonate weak acid DMPOH if it were present in large excess. Protonation of the μ_4-oxo group and all three py ligands would give copper(II) complex $(OH)Cu_4Cl_4(ODMP)_2{}^+$ (**XV**) with two anticipated properties as a cation. First, **XV** should have a more rigid molecular structure than $(\mu_4\text{-}O)py_3Cu_4Cl_4(ODMP)_2$. Second, it will surely coordinate at least one of the four $DMPO^-$ anions created by tetraprotonation of $(\mu_4\text{-}O)py_3Cu_4Cl_4(ODMP)_2$. This could give $(OH)Cu_4Cl_4(ODMP)_4{}^-$, which contains one $DMPO^-$ ligand for each copper(II) center. The larger $DMPO^-/Cu^{II}$ ratio in $(OH)Cu_4Cl_4(ODMP)_4{}^-$ compared to that in $(\mu_4\text{-}O)py_3Cu_4Cl_4(ODMP)_2$ might lead to the formation of phenol radicals, eqn. (16), which favors reaction (1a) at high DMPOH concentrations [4–6].

$$(OH)Cu_4Cl_4(ODMP)_4{}^- \longrightarrow (OH)Cu_3{}^{II}Cu^{I}Cl_4(ODMP)_3{}^- + DMPO^{\bullet} \quad (16)$$

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